CHANGES IN STRUCTURE AND CONTENT HUMIC SUBSTANCES IN SOIL DURING THE LABORATORY SIMULATED FIRES

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Research article

Abstract: The paper deals with the process of thermal degradation of humic substances in soil samples exposed to increased temperature. To determine the basic properties of humic substances, humic and fulvic acids are used conventional fractionation chemical laboratory methods. To determine changes in the chemical structure, the method of use of FT-IR ATR spectroscopy technique.

Keywords: Fire, soil organic matter, FT-IR spectrometry.

Introduction

Organic matter in the soil originates from natural plant, animal and microbial biomass and from man-made materials such as pesticides, hydrocarbons, plastics and industrial by-products. The components of soil organic matter range from living biomass to simple organic molecules (such as organic acids, aminoacids and carbohydrates) to complex polymers (humic substances) resulting from the decomposition of plant and animal materials in the soil. Humic substances are one of the most important fractions of the organic matter. They are dark coloured, heterogeneous, organic substances. The humic substances (HS) are usually split into humic acids (HA) and fulvic acids (FA). The relative amounts of these fractions are representative of the degree of humification. The progression of humification leads to the consumption of the most easily biodegradable components as carbon and energy sources conducting to condensation and oxidative reactions, finally resulting in more stable macromolecular structures Even though organic matter is usually present in relatively low concentrations (1 to 5 % in most mineral soils), it has a strong influence on soil properties due to its high surface area and high concentration of reactive sites (Chesworth 2008).

The effect of fire on the soil organic matter content is highly variable, and depends on several factors including fire severity and soil type. The impact of fires on soil organic matter include direct sterilization, production of fire-altered organic matter, formation of ash, charcoal, and modifications of the soil microflora and the whole trophic system i.e. changes in canopy.

Direct sterilisation

Only a small part of the heat generated during a forest fire is radiated to soil. The nature of the changes in soil depends on both the temperatures reached at different soil depths and the degree of heating that the different soil components can withstand before being altered. The degree of soil heating depends on factors such as the magnitude and duration of energy transferred from the fire to the soil, soil composition (including moisture), structure (porosity), etc. In general, below ground temperatures will rise very slowly due to the fact that dry soil is a very good insulator (DeBano, 2000), and to that in moist soils the evaporation of water will not allow a moist layer to go above the water boiling point (Campbell et al., 1995).

Soil inorganic and organic matter decomposition

During burning, a significant loss of organic matter may occur. Depending on the fire severity, observed impacts on the organic matter consist in slight distillation, charring, or complete oxidation (Certini, 2005). Irreversible heat-induced changes in soil properties occurs across a wide range of temperatures. For example, soil structure degradation occurs at 300 °C, organic matter loss occurs from

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100 °C until 450 °C, dehydroxylation and structural breakdown of clay minerals occur between 460 °C and 980 °C (DeBano, 2000).

Formation of charcoal and ash from biomass

The simplest model for soil biomass burning assumes that the ending products are H_2O, CO_2 and minerals contained in the ash. However, the complete oxidation of biomass requires conditions for oxygen availability during the combustion process which, in general, do not concur in nature. Under environmental conditions, the combustion is often incomplete and CO, CH_4, a complex range of pyrolysis products including hydrocarbons and particulate organic matter (OM) fractions are also produced. Exposure of biomass to temperatures > 150 °C induces dehydration and aromatic core formation, both leading to increased C and N content and decreased H and O content. Above 200 °C, the OM contains fewer O-alkyl structures, such as cellulose, and more aromatic C (Baldock and Smernik, 2002). Above 250 °C, a slight increase in the carbonyl region and a marked increase in the aromatic region of the FTIR spectra are observed. This enrichment in aromatic C results from preferential O-alkyl degradation and neoformation of aromatic structures (Almendros et al., 2003). Above 350 °C, polyaromatic compounds are formed (Paris et al., 2005).

Materials and methods

Sample collection and characterization

The field collection of soil samples was carried out at one point of delivery from the upper A genetic horizon to a depth of 30 cm in September 2009 in the former Botanical garden in Trnava. Collected soil sample was placed in polythene bags. After transport to the laboratory was soil treated in a standard way, namely free drying in a dark and dry place, crushing in a porcelain mortar, homogenization, sieving to the size below 2 mm. After that, all samples were detailed characterised by methods reported in Fiala (1999).

Laboratory heating experiments

The heat transfer by dry soil samples was investigated on laboratory apparatus containing a heating supply CLASSIC CLARE 4.0, voltmeter METEX M – 4640 with thermocouples (with a length of 1 cm, 2 cm, 3 cm) connected do PC. The temperature of the heated surface was adjusted to 250 °C and allowed to equilibrate. To the middle of the heated surface was placed a metal ring (15 mm thickness), which was filled with test soil sample, thermocouple was hoisted at 1, 2 and 3 cm from the heater. Then start recording layers of soil temperature measurements and which were recorded on a PC. The method is in accordance with EN 50281-2-1 (EN 50281-2-1: 1998).

The simulation of fire was carried out in laboratory oven/muffle furnace by exposing the samples of soil to the heat. The used temperatures were from 100 ºC to 900 ºC and constant 60 minutes duration. Samples were located in porcelain boats. They were filled up to approximately 0.5 cm with the exact weight of 10 grams. This is the standard procedure used in all our experiments, and is in compliance e. g. with Badía and Martí (2003) or Glass et al. (2008). After that, all samples were detailed characterised by methods reported in Fiala (1999).

Infrared spectroscopy

ATR-FTIR Spectrophotometric determinations were realized on Infrared Fourier Transform Spectroscopy with ATR technique – Attenuated Total Reflectance (Varian 660 Dual MidIR MCT/ TGS Bundle). Samples were directly applied to a diamante crystal of ATR and resulting spectra of them were corrected for background air absorbance. The spectra were recorded using a Varian Resolutions Pro and were measured in the region 4000–400 cm^{-1}; each spectrum was measured 36 times, at resolution 4. To minimize differences between spectra due to baseline shifts, the spectra were baseline corrected and ATR-corrected.

Result and discussion

Characterisation of the initial soil sample

The exchange pH value of the soil sample assumes a value of 7.3 (low-alkaline), what is typical for cultivated chernozem soil type on the calcareous loess occurring in Trnavská pahorkatina region. Total organic carbon content (3.141 mg/g) and humus content (5.42 %) is high, but the ratio of humic and fulvic acids carbon (C_{HA}/C_{FA} = 0.29) and color quotient ($Q_{4/6}$ = 3.86) indicate their worse quality. The degree of humification is very weak, takes the value of 9.23 %. Soil particle size analysis classified samples as sandy – loam soils.

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Transfer of heat by soil sample

The first experiment study was heat transfer in dry soil samples during potential fire. The thermal flow from hot surface through soil sample was measured at a distance of 1 cm (relatively stable about 200 °C), 2 cm (about 170 °C) and at a distance of 3 cm (below 100 °C). Deviations from continuous temperature increasing in soil samples are probably due to evaporation of water. The selected temperature of 250 °C to investigate the impact of fires on the SOM is relatively low, even in this experiment can be shown that the soil is relatively resistant to temperature increases and changes in the composition of SOM relate mainly to the surfaces of soil. Similar results were described by Humphreys and Craig (1981), which studied the soil temperature generated during different fire situations in Australian ecosystems. Less than 1 cm below the soil surface, the temperature only reaches 200 °C, under wildfire conditions whereas controlled burns reach only 125 °C and grasslands only 70 °C. By 2–3 cm, under their conditions, the soil temperature never exceeds the ambient temperature.

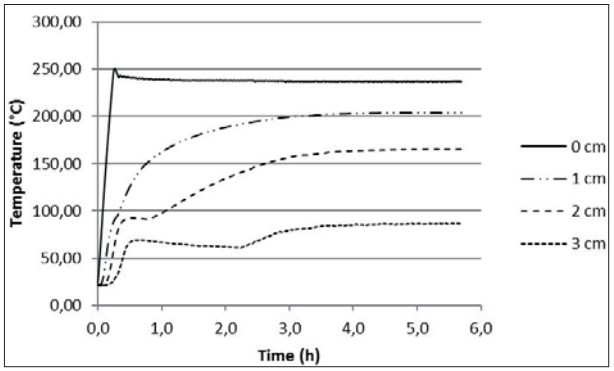

Fig. 1 Transfer of heat by dry soil sample

Quantitative changes in soil organic matter fraction (SOM)

In all tested soil samples the organic carbon content (C_{org}) have decreased significantly, depending on increasing temperatures, at 900 °C decrease of up to 98.73 %. The relative proportion of three main groups of SOM – non humine substances, humic and fulvic acids are shown in Fig. 2. On the decomposition of non humic substances is required a relatively low temperature. Non humic organic matter is represented by simpler organic compounds (e. g. sugars, proteins, lignin, fatty acids, alcohols, ethers, aldehydes, etc.) derived from plant and animal residues as well as intermediate products of microbial resynthesis. At present is appreciated their important role in soil process and the fertilization of soils, because they are very active, energy rich parts of the humus with significant effects on organisms, biological and chemical processes and the mobility of substances in the soil profile (Knicker 2005).

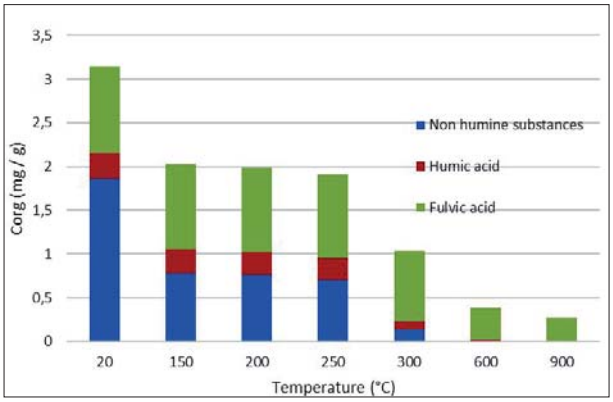

Fig. 2 The changes in proportion of main soil organic matter fractions

The humic and fulvic acid under 250 °C does not fundamentally alter. The content of non humine substances with the compare to the initial sample gradually decreased at temperatures up to 250 °C, where the loss of non humine substances was 62.36 %. Their significant decrease was occurred around 300 °C, where the presence of soil non humine substances was minimal and at 900 °C they absent. Most stable fraction of SOM to the increasing temperature are considered fulvic acids, what was confirmed by our experiments. Their content to the temperature about 300 °C did not change significantly, the loss was approximately 20 %. Significant decrease of fulvic acid (about 74 %) was observed at 900 °C. Humic acids degraded more rapidly. The total loss of humus substances at 900 °C was about 78.91 %. The analysis shows depletion and degradation of humic substances occurs at temperatures between 300 °C and 900 °C.

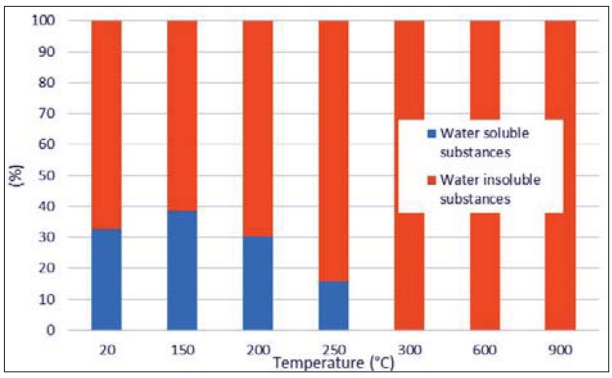

Fig. 3 The changes in proportion of water soluble and insoluble fractions

Tab. 1. The changes in proportion of soil organic matter fractions

Temperature [°C]	Total organic carbon [mg g^{-1}]	Carbon content of non humine substances [mg g^{-1}]	Carbon content of non humic acids [mg g^{-1}]	Carbon content of non fulvic acids [mg g^{-1}]	Carbon content of humine substances [mg g^{-1}]	Water soluble substances [%]	Water insoluble substances [%]
20	3.14	1.86	0.29	1.00	32.47	32.47	67.53
150	2.02	0.78	0.27	0.98	1.25	38.58	61.42
200	1.98	0.76	0.26	0.97	1.23	30.24	69.76
250	1.91	0.70	0.25	0.96	1.21	15.68	84.32
300	1.03	0.13	0.10	0.80	0.90	0.00	100.00
600	0.33	0.00	0.02	0.36	0.38	0.00	100.00
900	0.04	0.00	0.01	0.26	0.27	0.00	100.00

Fig. 3 shows loss of water-soluble and water-insoluble fractions of SOM. At temperatures up to 300 °C was observed a decrease proportion of water-soluble (more hydrophilic) organic substances, they are transformed to the water-insoluble (more hydrophobic) organic substances.

Quantitative changes in soil organic matter fraction (SOM)

Soil organic matter, especially the humic and fulvic components, has a high concentration of carboxyl (–COOH) and phenolic hydroxyl (–OH) groups. These groups are important because of their pH-dependent negative-charge character, which influences cation exchange reactions in the soil, and their ability to specifically bind certain metal cations. The ability of organic matter to bind metal cations decreases according to the following approximate order (Chesworth 2008): $Cu^{2+} > Ni^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$. Organic matter also contains positive charge sites, attributable predominantly to $–NH_2$ and aromatic –NH groups. Soil humic acid also has a significant hydrophobic character, which is attributable to aliphatic hydrocarbon chains in the humic structure. These hydrophobic binding sites strongly influence the retention of pesticides, hydrocarbons and organic industrial by-products in the soil. In Fig. 4 is spectrum of humic substances in range of wavenumber 400–1400 cm^{-1}. Presence of COOH groups was indicated by the peaks at 1117 to 1142 cm^{-1} which were attributed to the C–O stretches (Ahamadou 2013). Si-O vibrations of clay minerals were assigned at 1030 cm^{-1} as well as in our spectrum and from spectra in studies of Ahamadou et al. (2013) and D´Orazio et al. (2009). Peak near 900 cm^{-1} indicate presence of $CH=CH_2$ vibration.

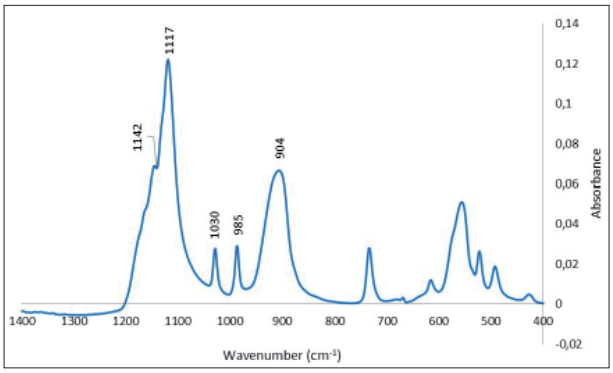

Fig. 4 Infrared spectrum of humic substances at 20 °C

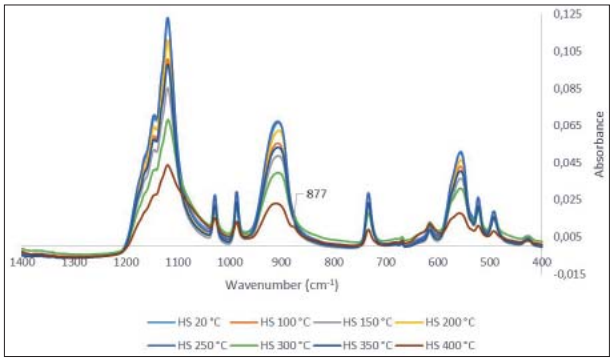

Fig. 5 Heated sample of humic substances

The heating of soil organic matter caused increase in aromaticity and the removal of oxygen-containing functional groups. The more recalcitrant and aromatic structures formed by fires derive from the alteration of carbohydrates, lipids, alkylated macromolecules and peptides. Consequently, some of these newly formed structures, initially non humified, can become substances like the humic fraction (Almendros et al., 1990; 2003; Baldock, J.A., Smernik, R.J., 2002. Fernandez et al., 1997, Gonzalez-Perez et al., 2004; Knicker et al., 2005).

In Fig. 5 are samples of humic substances after heating in same range as infrared spectrum of humic substances sample. In this region there are not any composition changes in humic substances, all significant peaks are preserved. Despite this fact, at wavenumber 877 cm^{-1} can be seen small peak in spectrum of HS sample heated at 400 °C, indicated $C=CH_2$ vibration in compare sample at 20 °C.

In infrared spectrum of **humic acid** are presented absorbance band of hydroxyl-, carboxyl-, phenolic-, amine- and carbonyl-bands (Fig. 6). Broad bands between 3650 and 3050 cm^{-1} indicated the presence of hydroxyl groups O–H. The doublet between 2876 and 2912 cm^{-1} represent C–H stretching of methyl and methylene groups of aliphatic and non-strained cyclic hydrocarbons (Giovanela et al. 2010), the 1631 cm^{-1} band is assigned to aromatic C=C double bonds conjugated with C=O and/or COO– (Laride 2015). An intense band around 1128 cm^{-1} is assigned to alcoholic and polysaccharide C–O stretch and O-H deformation (Sakellariadou 2006).

At higher temperatures (Fig. 7), the bands of O-H were significantly decreased. The loss of water is followed by the release of carbon monoxide and dioxide, e.g., decarboxylation at higher temperatures.

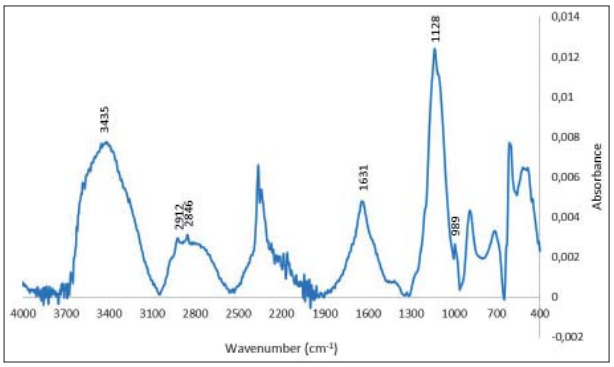

Fig. 6 Infrared spectrum of humic acid at 20 °C

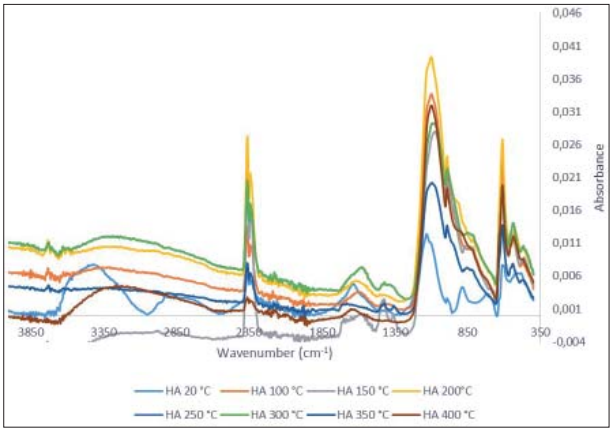

Fig. 7 Heated sample of humic acid

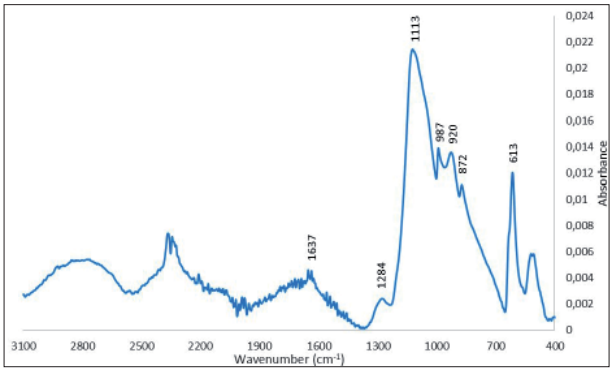

Fig. 8 Infrared spectrum of fulvic acid at 20 °C

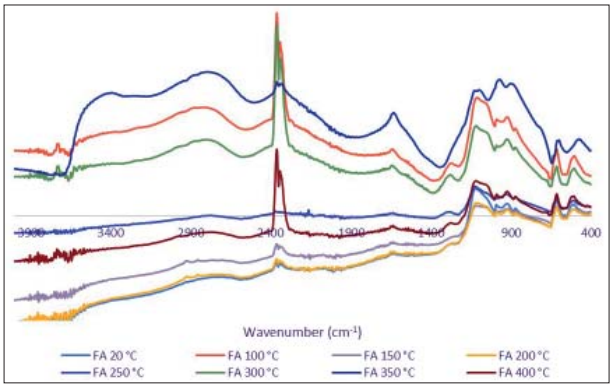

Fig. 9 Heated sample of fulvic acid

Infrared spectrum of **Fulvic acid** is in the Fig. 8. Absorption bands at 1637 cm^{-1} likely correspond to the C–O stretching vibration in amide I and both N–H bending and C–N stretching in amide II. The absorption bands in the spectra of the fulvic acid fraction in the region 800–400 cm^{-1} arise from organic components, mainly substituted benzene nuclei, as well as condensed aromatic rings. Absorption band at 613 cm^{-1} possibly arise from the C–C vibrations in para-substituted or mono-substituted aromatic rings (Naidja 2002). Region of wavenumber about 2940–2900 cm^{-1} is assigned to aliphatic C–H stretching. Range of wavenumber from 900 to 600 cm^{-1} is significant for presence of C–H deformation of aromatic rings with various substitutions (Liu 1997).

Both FA and HA seem to be resistant to the temperature effects (Fig. 9). Even after being heated to 400 °C the materials retain most of their original FT-IR spectra features. However, in Fig. 9 can be seen increasing of peaks near 900 to 600 cm^{-1} indicated C–H compared with 1110 cm^{-1} C–H in aromatic rings. As well as, with increasing temperature O–H bands are missing in spectrum.

Conclusion

Realized experiments show the major changes in soil organic matter due to rising temperatures. Changes were quantitative and qualitative. Firstly, non humic substances are degraded followed by decomposition of humic substances to fulvic acid with lower quality. The total mineralization of soil organic matter is occurring after that. Thermal treatment of initial soil represented wildfires indicated that upon heating, the carboxyl content in humic substances decreases whereas aliphatic decreases and aromatic increases. These processes has significantly affect to soil quality and can affect the transport of nutrients or pollution through soils.

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References

AHAMADOU, B.; HUANG and Q.; YAPING, L.; IQBAL, J. (2013): Composition and structure of humic substances in long-term fertilization experimental soils of southern China. *Journal of Soil Science and Environmental Management*, 4, p. 77–86.

ALMENDROS, G. et al. (2003): Rearrangement of carbon and nitrogen forms in peat after progressive isothermal heating as determined by solis – state ^{13}C- and ^{15}N-NMR spectroscopies. *Organic Geochemistry*, 34, p. 59–68.

ALMENDROS, G.; GONZALEZ-VILA, F.J.; MARTIN, F. (1990): Fire-induced transformation of soil organic matter from an oak forest: an experimental approach to the effects of fire on humic substances. *Soil Science*, 149, 158–168.

BADÍA, D.; MARTÍ, C. (2003): Plant ash and heat intensity effects on chemical and physical properties of two contrasting soils. *Arid Land Research and Management*, 17, p. 23–41.

BALDOCK, J.A.; SMERNIK, R.J. (2002): Chemical composition and bioavailability of thermally, altered Pinus resinosa (Red Pine) wood. *Organic Geochemistry 33*, p. 1093–1109.

CAMPBELL, G.S.; JUNGBAUER JR, J.D.; BRISTOW, K.L.; HUNGERFORD, R.D. (1995): Soil temperature and water content beneath a surface fire. *Soil Science*,159, p. 363–74.

CERTINI, G. (2005): Effects of fire on properties of forest soils: a review. *Oecologia 143*, p. 1–10.

CHESWORTH, W. (2008): *Encyclopedia of soil science*. Springer, Berlin. 902 p. ISBN 978-1-4020-3995-9.

D'ORAZIO, V.; SENESI, N. (2009): Spectroscopic properties of humic acids isolated from the rhizosphere and bulk soil compartments and fractionated by size-exclusion chromatography. *Soil Biology and Biochemistry*, 41, p. 1775–1781.

DeBANO, L.F. (2000): The role of fire and soil heating on water repellency in wildland environments: a review. *Journal of Hydrology*, 231–232, P. 195–206.

FERNANDEZ, I.; CABANEIRO, A.; CARBALLAS, T. (1997): Organic matter changes immediately after a wildfire in Atlantic forest soil and comparison with laboratory soil heating. *Soil Biology and Biochemistry 29*, 1–11.

FIALA, K. et al. (1999): *Mandatory methods of soils analysis*. Bratislava: VÚPOP Bratislava. ISBN 80-85361-55-8.

GIOVANELA, M.; PARLANTI, E.; SORIANO-SIERRA, E.J.; SOLDI, M.S.; SIERRA, M.D. (2004): Elemental compositions, FT-IR spectra and thermal behavior of sedimentary fulvic and humic acids from aquatic and terrestrial environments. *Geochemical Journal*, 38, p. 255–264.

GLASS, D.W.; JOHNSON, D.W.; BLANK, R.R.; MILLER, W.W. (2008): Factors affecting mineral nitrogen transformation by soil heating: a laboratory – simulated fire study. *Soil Science*, 173, 6, p. 387–400.

GONZÁLEZ-PÉREZ, J.A.; GONZÁLEZ-VILA, F.J.; ALMENDROS, G.; KNICKER, H. (2004): The effect of fire on soil organic matter – a review. *Environment International 30*, 6, p. 855–870.

HUMPHREYS, F.R; CRAIG, F.G. (1981): Effects of fire on soil chemical, structural and hydrological properties. In: Gill AM, Groves RH, Noble IR, editors. *Fire and the Australian Biota*. Canberra, Australia: Australian Academy of Science. p. 177–200.

KNICKER, H.; GONZALEZ-VILA, F.J.; POLVILLO, O.; GONZALEZ, J.A.; ALMENDROS, G. (2005): Fire – induced transformation of C- and N-forms in different organic soil fractions from a Dystric Cambisol under Mediterranean pine forest (Pinus pinaster). *Soil Biology and Biochemistry 37*, 701–718.

LARIDE, W.A. (2015): Infrared Spectra of Humic Acid and MetalHumates Precipitated from Groundwater. *Journal of Water Resource and Hydraulic Engineering*, 4, 1, p. 105-110.

LIU, X.; RYAN, D.K. (1997): Analysis of Fulvic acids using HPLC/UV coupled to FT.IR Spectroscopy. *Environmental Technology*, 18. p 417-424.

NAIDJA, A.; HUANG, P.M.; ANDERSON, W.; KESSEL, C. (2002): Fourier Transform Infrared, UV-Visible, and X-ray Diffraction Analyses of Organic Matter in Humin, Humic Acid, and Fulvic Acid Fractions in Soil Exposed to Elevated CO_2 and N Fertilization. *Applied Spectroscopy*, 56, 3.

PARIS, O.; ZOLLFRANK, C.; ZICKLER, G.A. (2005): Decomposition and carbonisation of wood biopolymers – a microstructural study of softwood pyrolysis. *Carbon 43*, 53–66.

SAKELLARIADOU, F. (2006): Spectroscopic studies of humic acids from subsurface sediment samples collected across the Aegean Sea. Mediterranean Marine Science, 7/2, p.11–17.